A NEW METHOD FOR STANDARDIZED CALIBRATIONS OF ELECTROCHEMICAL CONCENTRATION CELL OZONESONDES

F. J. Schmidlin[1], B. A. Hoegger[2], G. Levrat[3], T. M. Baldwin[1], G. Brothers[1]

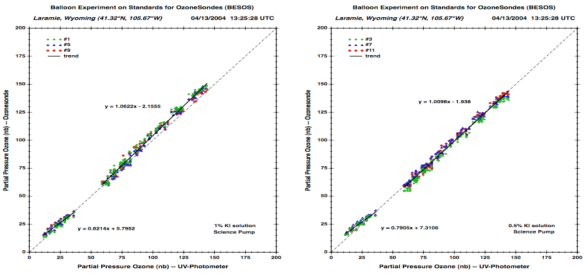
1) NASA/Goddard Space Flight Center, Wallops Island, Virginia
2) Bruno Hoegger Scientific consulting, Marly, Switz.
3) MeteoSwiss Aerological Station, Payerne, Switz.

Precise and repeatable ECC preparation is made possible with the NASA/ GSFC"Digital Preparation and Calibration Workbench," recently put into operational use. This computer controlled ozonesonde workbench follows the same sequence of ECC preparation manually employed. The 'reference calibration standard' permits simultaneous preparation of two ECC units. Performance of ECC is digitally monitored making comparison of different combinations of potassium iodide (KI) solution concentrations possible. This capability encouraged us to compare 2.0, 1.5, 1.0, and 0.5 percent KI concentrations against known reference values of ozone partial pressure.

In the past, ECC accuracy was quantified through *in situ* comparisons, an expensive method for obtaining such comparisons. Laboratory tests at the World Ozone Calibration Facility in Jülich, Germany were useful (Smit et al, 2007) and the occasional gaint-balloon flights such as BOIC, STOIC, and BESOS provided additional performance information.

BESOS, or Balloon Experiment on Standards for Ozonesondes, (Deshler et al, 2008) was carried out in April 2004 and included Science Pump, Inc. (SPC) and EnSci ECC's. A UV photometer was included as a reference. Comparison of KI concentration of 0.5 percent agreed better with the photometer.

SPC ECC ozonesondes have been used at NASA Wallops since 1970. Therefore, performance evaluation applies only to the SPC ECC. The correlation graphs below show the level of agreement between a reference photometer and the ECC's with 1.0 percent (left) and 0.5 percent (right) KI solutions. Only the data between 50hPa and 150 hPa are considered. The correlation of the ECC with 0.5 percent KI and photometer is very good, however, the sample size is small, three instruments.



Digital Reference Calibration Facility

Manual insertion of KI solution is required

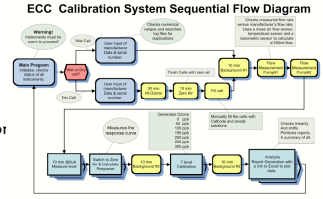
Development completed in late 2007.

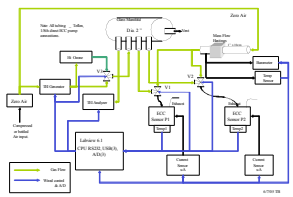
All functions are computer controlled.

Digital record is available.

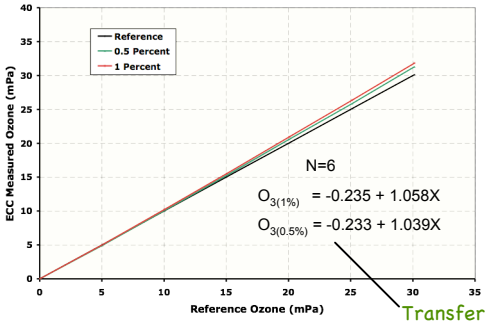
The system consists of a computer, mass flow meter, TEI 49C ozone generator, TEI 49C ozone analyzer, and incidental equipment.

To insure accurate and reliable calibrations, the TEI generator and analyzer are calibrated each month using a primary standard, our 3-meter long-path photometer.





Zero-grade air is introduced into the system's TEI O_3 generator where various and controlled levels of ozone are produced. Ozone is distributed simultaneously to the ECC cells and TEI O_3 analyzer (Reference Ozone). Comparison of the ECC and TEI readouts are discussed below.



Calibration showed an apparent linear increase of the 1.0 % and 0.5 % KI solutions relative to the reference.

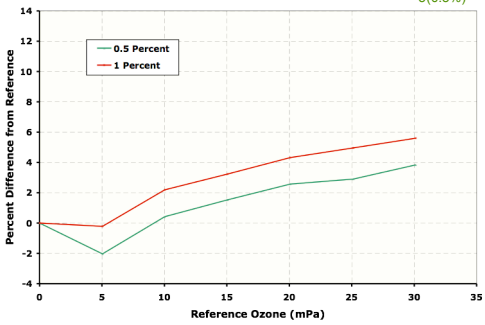
WHY?

ECC measures more ozone than the reference.

WHY IS THIS POSSIBLE?

Transfer function to convert from 1% to 0.5% KI

$$O_{3(0.5\%)} = -0.233 + 1.039\,[(O_{3(1\%)} + 0.2354)/1.058]$$

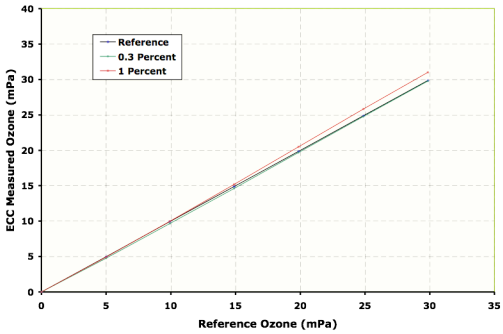


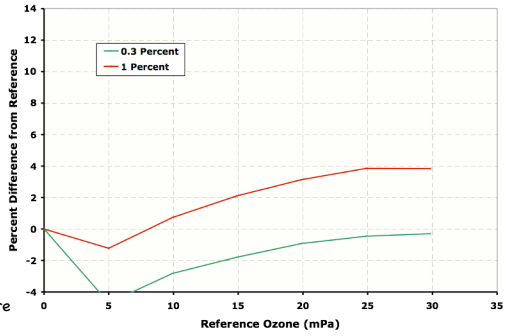
Absolute-percent differences revealed ECC measurement is not linear.

WHY?

There is no immediate answer to the questions WHY. We might speculate that perhaps the answer lies with the assumption that the ozone equation expects the transfer of two electrons for every molecule of ozone consumed in the cathode solution; perhaps the 'ideal stoichiometry equation is 'per sé' not applicable. Or, could the solution pH be a factor in the mico-titration, as suggested by Barnes (1982).

Tests with the 'reference calibration standard' of 2.0, 1.5, 1.0, and 0.5 percent KI concentrations suggested that agreement with the reference calibration improved with lower KI concentrations. This suggested that a lower concentration might reach better agreement with the reference. The figures below show this was the case.





All test data obtained with the reference calibration facility showed negative differences in measured ozone between the ECC and reference at 5 mPa . Until additional information becomes available we feel this feature exists because low ozone amounts are not being handled well by the ECC, or possibly the reference needs further scrutiny.

Although, it appears the 0.5 % solution might be a better choice to use with the Science Pump ECC, additional testing with different KI concentrations are planned.

Barnes, R. A., 1982: The accuracy and precision of electrochemical concentration cell ozonesondes. Ph.D Thesis, Drexel University

Deshler, T., et al, 2008: Atmospheric comparison of electrochemical cell ozonesondes from different manufacturers, and with different cathode solution strengths. J. Geophys. Res., 113, D04307, doi:10.1029/2007JD008975.

Smit, H.G.J., et al, 2007: Assessment of the performance of ECC-ozonesondes under quasi-flight conditions in the environmental simulation chamber: Insights from the Juelich Ozone Sonde Intercomparison Experiment (JOSIE). J. Geophys. Res., 113, D13302, doi:10.1029/2007JD009091.